

Innovations

A Sensitive Technique for Measuring Hydroxyl Radicals, Atmospheric Cleansing Molecules

The hydroxyl radical (OH) is so small that 10 billion billions would fit in a raindrop. Despite its diminutive size, OH is probably the single most important cleansing agent in the earth's atmosphere. Countless trillions of these molecules continually purge the atmosphere of a wide variety of pollutants, including carbon monoxide, methane, and nitrogen dioxide. As more and more compounds are released into the atmosphere, an accurate understanding of the role played by OH becomes increasingly important. But, before scientists can gain that understanding, they must first be able to measure the hydroxyl radical with precision.

Formed in the atmosphere by a photochemical reaction, OH radicals last only about a second before reacting with some other chemical species. This highly reactive nature is what makes OH such an important cleansing agent. Unfortunately, it also makes OH extremely difficult to measure. The molecule is small, very reactive, and although constantly replenished during daylight hours, precious little of it exists at any given place and time. Concentrations are typically so low (in the parts per quadrillion range) that accurate measurement of the hydroxyl radical has eluded researchers for nearly two decades.

Recently, Fred Eisele, an atmospheric scientist at the Georgia Tech Research Institute in Atlanta, successfully demonstrated a powerful new OH measurement

technique. Unlike earlier methods, which used lasers and were plagued by high background interference, Eisele's technique uses extremely sensitive mass spectrometry, a radical concept that could revolutionize OH measurement methodology. The new system is fast, accurate, reliable, and highly portable.

A Surprising Discovery

In the early 1980s, Eisele's research group developed an extremely sensitive atmospheric ion measurement technique. Their pioneering efforts resulted in the first ground-level mass spectrometric measurements of atmospheric ions in 1983, followed by the first tandem-mass spectrometric identification of tropospheric ions three years later. Eisele's novel OH measurement technique grew out of this highly successful program.

During the summer of 1987, Eisele and research technician David Tanner were measuring ions being formed under high-voltage DC power lines near Pittsfield, Massachusetts, when they made a surprising discovery. The investigators had moved their mobile mass spectrometer away from the power lines for a series of background measurements. While routinely sweeping through the negative spectrum, Eisele noticed a large sulfuric acid peak that exhibited drastic variations in concentration on extremely short time scales.

"The numbers dropped dramatically whenever a cloud passed in front of the sun," recalls Eisele. "Moreover, the signal rose to a maximum during the day, but fell to nearly zero when the sun set."

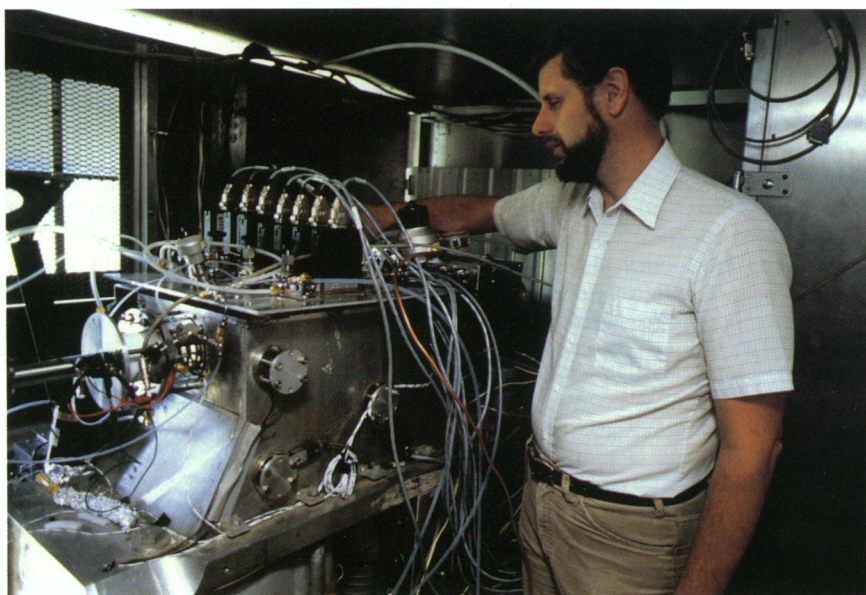
Such strong solar and diurnal fluctuations were significant. "We suddenly realized that the only mechanism which explained our observations was that OH was reacting with sulfur dioxide to form sulfuric acid," says Eisele. "As the OH concentration rose and fell with the amount of incident sunlight, corresponding changes occurred in the amount of sulfuric acid. So the production of sulfuric acid was directly tied to the OH concentration. We later realized we might have discovered a totally new technique for measuring OH."

Eisele knew that the sulfuric acid he was measuring depended on the prevailing OH concentration. Although he could specifically measure the amount of naturally occurring sulfuric acid, he had no way of determining either the formation rate or removal rate due to the presence of numerous interfering reactions in the complicated natural environment. If he could artificially duplicate the same sequence of atmospheric events under carefully controlled conditions, however, he should be able to precisely determine the OH concentration.

A Novel Method

Deep in a forest 50 miles north of Atlanta, Eisele confirmed his theory and demonstrated the feasibility of his newly proposed ion-assisted OH measurement scheme. By manually injecting sulfur dioxide into an existing air sampling tube, Eisele converted the ambient hydroxyls into sulfuric acid, which he then ionized and measured with the mass spectrometer.

Even this first brief attempt showed reasonably clear diurnal variations in the artificially generated sulfuric acid concentration, reflecting the ever-changing levels of OH. But there was much more work to be done. For the next several years, Eisele and Tanner steadily worked to perfect the technique. They modified the front end of their sampling apparatus to support the physical chemistry needed to specifically detect the OH radical. They enhanced the flow-tube dynamics and installed a more effective ionization source capable of introducing high concentrations of a single specific ion species into the OH flow tube. They also reduced background interferences, improved the measurement speed, and developed more reliable calibration methods.



Measuring OH *in situ*. Fred Eisele in his mobile laboratory.

Work in the lab was augmented with field measurements on Sapelo Island off the Georgia coast and on Mauna Loa, a Hawaiian volcano. "The Mauna Loa site provided an opportunity to sample a more stable and much cleaner air mass," says Eisele, "enabling us to better understand and remove background interferences."

Unlike other OH measurement schemes, Eisele's technique relies on the inherent sensitivity of atmospheric pressure chemical ionization/mass spectrometry. "We can measure ions in very low concentrations—easily in the parts per quintillion range—because they possess an electric charge, having gained or lost an electron," explains Eisele. "With the mass spectrometer we can identify ions at concentrations as low as one per cubic meter."

OH, however, is a neutral species: it has no charge. "If it had a charge, we could manipulate it with electric fields, selectively concentrating it or discriminating against it," says Eisele. "And we would be able to measure it directly with the mass spectrometer. But lacking a charge, we can't touch it. To be measured, the hydroxyl must first be converted into an ion that we can detect with our instrument."

Eisele's revolutionary method begins by drawing ambient air through a special sampling tube designed to maintain laminar flow. The center of the flow, where the requisite chemical reactions occur and measurements are taken, is shielded by the surrounding sheath of air from all equipment surfaces which could destroy OH on contact.

Shortly after entering the sampling tube, the middle of the flow is made turbulent by the injection of nitrogen "buffer" gas containing a small amount of isotopically labeled sulfur dioxide (SO_2). The SO_2 quickly mixes with the air sample and reacts with entrained OH to form HSO_3 . This titration reaction converts all the OH initially present in the center of the tube into isotopically labeled HSO_3 . The HSO_3 then quickly reacts with O_2 and H_2O (both already present in the air sample) to form sulfuric acid (H_2SO_4).

But additional OH is continually being formed from a reservoir species, HO_2 , contained in the air sample. To prevent this newly created OH from reacting with SO_2 and skewing the measurement, Eisele adds a heavy dose of propane shortly after all the initial OH is titrated. The propane removes any additional OH that might be formed by the cycling of HO_2 back into OH.

The resulting concentration of sulfuric acid is then measured with a chemical ionization method. In an isolated high-pressure source, gas phase nitrate ions (NO_3^-)



Sunrise at Sapelo Island. The solar tracker correlates changes in OH concentration to incident solar flux.

are prepared and forced by electric fields into the titrated air sample. These ions react with the sulfuric acid to form bisulfate ions (HSO_4^-) and nitric acid (HNO_3). By measuring the relative concentrations of nitrate ions and isotopically labeled bisulfate ions with the mass spectrometer, and by using the reaction rates and times involved, Eisele can accurately determine the amount of artificially generated sulfuric acid. Since the OH initially present is converted one-for-one into sulfuric acid, the amount of isotopically labeled sulfuric acid also reveals the ambient OH concentration.

Eisele's technique promised a radically new and highly sensitive OH measurement capability. But was it accurate enough to permit scientists to begin testing their photochemical models?

Informal Comparison

To determine the accuracy of his technique, Eisele collaborated with scientist George Mount at the Aeronomy Laboratory of the National Oceanic and Atmospheric Administration in Boulder, Colorado. While Eisele had been developing his ion-assisted chemical analysis method to measure OH, Mount had been pursuing the same goal with a totally different approach—one that recognized the hydroxyl radical's unique spectroscopic fingerprint through long-path laser absorption. To test their two dissimilar techniques, the researchers decided to hold an informal comparison at NOAA's Fritz Peak Observatory in the Colorado Rockies during the summer of 1991.

Other than geography, the two techniques had little in common. Unlike Eisele's chemical analysis technique, Mount's optical method relies on absorp-

tion spectroscopy of the hydroxyl radical. Although not as sensitive, Mount's technique is simpler and more direct.

To measure OH, Mount's technique sends a collimated ultraviolet laser beam to a 121-element retroreflector array located across a mountain valley 10.3 km away. The reflected light is collected by a Cassegrain telescope at the observatory and focused on the entrance slit of a high-resolution spectrograph. The amount of OH absorption over the total 20.6 km optical path is then determined, and the molecule's concentration calculated.

Despite the differences in the two techniques, Eisele and Mount found surprisingly good agreement in their results, lending strong credibility to both techniques. Most of the time, measured values of OH concentration agreed within the limits of errors of the two instruments. Of the few times when the data differed sharply, several instances were attributed to local fluctuations in the amount of incident sunlight or measurements being taken in different air masses. A few of the times the differences simply could not be explained, which emphasizes the need for more extensive studies.

"Our mobile laboratory, which measures OH *in situ*, was located near Mount's retroreflector array," says Eisele. "Any variations in OH along Mount's optical path—caused by the passage of a small cloud overhead, for example—would naturally show up as discrepancies in our data."

For the first time, there was sufficient confidence in the accuracy of their OH measurements that the scientists could use them to test existing photochemical models.

An Unknown Scavenger

When the researchers' numbers were plugged into the models, there were some surprising results.

"The model predictions were up to three to four times higher than what we had measured," says Eisele. "In the past, we probably would have assumed that the model was right and the measurement was wrong. The fact that our different measuring techniques had agreed, however, suggested that neither technique was in error by very much."

But, if both models and measurements were assumed correct, where was the missing OH?

Eisele, Mount, and other NOAA researchers have postulated the presence of an unknown hydrocarbon scavenger of OH. The yet-to-be identified compound was likely reacting with the hydroxyl, significantly reducing the ambient concentration.

"Our measured OH concentrations could also have been suppressed somewhat because we were measuring at, or very near, ground level," says Eisele. "The Colorado site was a fairly complex environment to measure in. We may have been seeing a ground surface effect caused by hydrocarbon emissions from the surrounding forest."

Measurements performed last summer at Mauna Loa may help clear up the mystery of the missing radical and further confirm Eisele's unique measurement technique. In conjunction with the Mauna Loa Observatory Photochemistry Experiment, a study sponsored by the National Center for Atmospheric Research, Eisele and Tanner took their instrument to Hawaii for their second field measurement at the site. In addition to performing a number of important photochemistry experiments, the Mauna Loa study measured the concentrations of a number of hydrocarbons, nitrogen compounds, and a variety of other compounds found in the troposphere.

"Unlike the Colorado site, Mauna Loa offers a much simpler environment with far fewer trees and much cleaner air," says Eisele. "So there is a much better chance that we measured all the major species which

were reacting with OH. Therefore, the photochemical models should be able to reasonably predict the amount of OH, and this value should agree with our measurements."

The Mauna Loa data have recently been compiled and soon will be analyzed. The researchers anxiously await the results.

Looking Ahead

Eisele has continued to improve both the accuracy and the sensitivity of his instrument. During the 1991 comparison, his device was capable of measuring OH at the 1×10^5 molecules/cm³ range with a 300-second integration time. The instrument can now measure in the $2-3 \times 10^4$ molecules/cm³ range with a 1 hour integration time—a detection sensitivity which offers the exciting possibility of measuring nighttime OH concentrations (a feat which may have recently been accomplished).

An early spin-off of Eisele's work on the OH radical, his development of a high-pressure selected ion chemical ionization mass spectrometric technique, has allowed him to identify and measure a variety of heretofore inaccessible but potentially significant compounds.

"OH reacts with things like sulfur dioxide and dimethylsulfide to form compounds like sulfuric acid and methanesulfonic acid," says Eisele. "These have been the most likely candidates to either form new particles or to grow preexisting particles into larger particles that eventually become condensation nuclei in clouds."

The number of these particles determines how many droplets are in a cloud, says Eisele. "If you have more condensation nuclei, you have more little drops; if you have less, you have fewer big drops. The number and size of the droplets affects the reflectance properties of the clouds, and thus the albedo over much of the earth's surface. Because droplet formation is limited by the number of condensation nuclei, we need to know how many there are, and we need to understand how they

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are being formed." Eisele and Tanner continue to pursue these measurements.

Meanwhile, the search for other hydrocarbon compounds as possible scavengers of OH continues. A second tropospheric OH comparison is scheduled at NOAA's Fritz Peak Observatory later this summer. In addition to Mount and Eisele, other NOAA scientists will be there measuring nonmethane hydrocarbons and many other species of potential interest. A third OH measurement technique, based on laser-induced fluorescence, will be tested as well. Like the one conducted in 1991, this summer's field study will be a serious, but informal, attempt to compare OH measurement methodologies and use the resulting data as input into photochemical models.

A better understanding of the elusive hydroxyl radical will help scientists better understand the complex photochemical reactions occurring in the atmosphere. This, in turn, may help clear up some of the mysteries that surround such major issues as high tropospheric ozone levels and global warming.

James E. Kloeppel

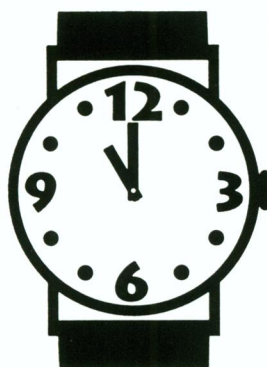
Suggested Reading

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